

## PATENT SPECIFICATION

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## (54) PROCESS FOR SIZING AND DYEING WARPS OF CELLULOSE FIBRES

(71) We, HOECHST AKTIENGESSELLSCHAFT, a body corporate organised according to the laws of the Federal Republic of Germany, of 6230 Frankfurt/Main 80, Federal Republic of Germany, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process for sizing and dyeing warps of cellulose fibres.

For the preparation of woven cotton fabrics having a dyed warp and undyed weft, so-called 'denim' materials, two different sizing-dyeing processes, using coupling and diazo components for the formation of azo dyestuffs on the fibres, have been proposed.

In the first process, the warp is padded with a sizing liquor which contains, in addition to the sizing agent, an alkaline dissolved coupling component (C.I. Azoic Coupling Component). After drying the warp on drying cylinders, the warp is woven with an undyed (unbleached white) weft yarn; the fabric is then padded on a foulard with an acid solution of a diazonium salt (C.I. Azoic Diazo Component), thus effecting formation of the dyestuff by coupling on the fibre.

In the second process, the sizing liquor contains an alkaline dissolved coupling component and also an alkali-resistant stabilized diazo compound, for example a triazene or anti-diazotate, which does not couple in the alkaline medium. After drying and weaving the warp, the dyestuff is formed by an acid or neutral steaming process. In this process the acid developing bath is not necessary. Compared with the first process the second is, therefore, simpler, but it is more expensive because of the use of stabilized diazo compounds.

The present invention provides a process for sizing and dyeing a warp comprising cellulose fibres, which comprises applying to the warp a hot alkaline aqueous liquor containing an azo dyestuff coupling com-

ponent, an anionic protective colloid, a finely dispersed aromatic amine, and sodium nitrite, drying the warp, and subsequently applying to the warp a hot aqueous liquor containing a sizing agent, an anionic wetting agent, and a weak organic carboxylic acid or an inorganic salt that hydrolyses to give an acidic reaction.

According to the invention, the warp-sizing-dyeing process can be effected in a simple, secure and economical way by using a hot liquor containing an alkaline dissolved coupling component (C.I. Azoic Coupling Component), alkali, an anionic protective colloid, sodium nitrite and a fine dispersion of an aromatic amine (C.I. Azoic Diazo Component), but not containing a sizing agent; this liquor is generally applied by padding. The warp is then padded with a hot sizing liquor on a foulard of a sizing machine, the sizing liquor containing, in addition to one or more sizing agents, a weak organic carboxylic acid, optionally one or more of its alkali metal salts, and an anionic wetting agent, whereby development of the azo dye on the cellulose fibre is effected by diazotization of the amine and coupling of the formed diazonium compound with the coupling component; afterwards the warp is dried.

The process of the invention may be used in the preparation of cellulose fibre fabrics consisting of dyed warp threads and untreated or differently dyed weft yarns.

Suitable coupling components (Azoic Coupling Components) are, for example, low or medium-substantive arylamides of acetoacetic acid, or 2 - hydroxynaphthalene - 3 - carboxylic acid or of heterocyclic o - hydroxycarboxylic acids. There may be mentioned for example, 2 - hydroxynaphthalene - 3 - carboxylic acid - phenylamide and its derivatives which are substituted in the arylamide radical by alkyl or alkoxy groups or chlorine atoms, for example 2 - hydroxynaphthalene - 3 - carboxylic acid - (2'-methyl - phenyl - 1') - amide, 2 - hydroxynaphthalene - 3 - carboxylic acid - (2'-

methoxy - phenyl - 1') - amide and 2-hydroxynaphthalene - 3 - carboxylic acid - (3' - chloro - 6' - methoxy - phenyl - 1') - amide; furthermore 2 - hydroxycarbozol-3 - carboxylic acid - (4' - chloro - phenyl - 1') - amide, 5 - chloro - 2 - acetylamin-1,4 - diethoxy - benzene and 4,4' - bis-(acetoacetylamin-3,3' - dimethyl - diphenyl.

10 Suitable amines (C.I. Azoic Diazo Components) are, for example: 4 - nitro - 2-amino - 1 - methyl - benzene, 5 - nitro - 2-amino - 1 - methoxy - benzene, 2 - amino - 1 - methoxy - benzene - 4 - sulfonic acid-15 - butylamide, 1 - amino - 2,5 - dimethoxy - benzene - 4 - nitrile, 1 - amino - 4-benzoylamino - 2,5 - diethoxy - benzene, and 4,4' - diamino - 3,3' - dimethoxy - diphenyl.

20 The dispersions of the aromatic amines (base-dispersions) used in the process of the invention can be prepared in a number of different ways:

25 The dispersion can be obtained, for example, by grinding the amine in an aqueous paste, in the presence of a dispersing agent in order to avoid agglomeration. This operation can be effected in a rolling or vibrating mill using balls; particularly suitable devices 30 are stirring ball mills which contain glass beads or natural sand. A fine dispersion obtained with a so-called dissolver unit also often leads to acceptable results.

35 Another method is to add to water a solid preparation which has been prepared by spray-drying a base-dispersion containing a solid dispersing agent or by grinding, for example in a disk attrition mill, a mixture of a solid dispersing agent and the amine.

40 It is also possible to prepare the dispersion in the padding liquor, for example by adding to the aqueous padding liquor a solution of the amine and of a dispersing agent in a water-soluble organic solvent.

45 The dispersing agents used must be compatible with the alkaline solution of the coupling component and with its stabilizing surface active agent, and must, therefore, be anion-active. As examples of suitable dispersing agents there may be mentioned: 50 alkylarylsulfonates, arylsulfonates, sulfonated cresol - formaldehyde resins, formaldehyde-naphthalene sulfonic acid-condensation products, lignine sulfonates and oxylignines.

55 The maximum particle size of the dispersed amine should be 0.03 mm or smaller; the so-called "medium particle size", according to Ramler-Rosin, should be 0.003 mm or smaller.

60 Such a dispersion can, for example, be prepared as follows: 173 parts by weight of water-moist 78% 4,4' - diamino - 3,3' - dimethoxy - diphenyl together with 45 parts by weight of an oxylignine are added portion- 65 wise, whilst stirring, to 82 parts by volume

of water. The mixture obtained is then ground until the necessary fine dispersion is obtained in a continuously operating ball mill provided with a stirrer and charged with silicartzite beads (zone-less discharge of a dilution 1:40 applied to filter paper having medium pore width).

The mol-proportion of amine to coupling component used is generally, for economic reasons, in the range of from 1.2 to 1.5:1. The quantity of alkali nitrite used is related to the amount of amine, and is generally from 200 to 300% of the theoretical amount required.

Any of the usual sizing agents can be used. In addition to starch, which is mainly used for this purpose, carboxymethyl-cellulose may also be mentioned as a suitable sizing agent.

Suitable acids which may be used are, for example, formic acid, acetic acid, lactic acid, tartaric acid and succinic acid. It is also possible to use an inorganic salt that hydrolyses to give an acidic reaction, for example aluminium sulfate.

In order to obtain denim goods having the desired firm feel it is possible to effect a drying process after this treatment with an acid medium, optionally after an air- 90 passage in a suitable drying installation, for example a cylinder drying machine, a tenter dryer or a hotflue. In order to remove surplus size, dye auxiliaries and residues after the dyestuff formation, the goods may be washed and then dried in the usual 100 manner.

The principle of the process of the invention comprises, in a preferred version, padding cotton warps with a hot liquor which does not contain any sizing agent, but contains an alkaline agent, an alkaline dissolved coupling component, a fine dispersion of an aromatic amine (C.I. Azoic Diazo Component) and sodium nitrite. After drying the warps on drying cylinders, development of the insoluble azo dyestuff on the cellulose fibre is effected by overpadding with a sizing liquor containing a weak organic acid, which may be buffered with one of its alkali metal salts, an anionic wetting agent, and one or more sizing agents. The development is effected before the weaving the warps with unbleached white weft yarns. The passage in the acid medium causes no detachment of parts of the sized warps. The aftertreatment is effected, as usual for piece goods with such developing dyes, on a full width washing machine by alkaline soaping and rinsing at boiling temperature.

The use of dispersed (non-diazotized) aromatic amines offers the advantage that these dispersed or dispersable bases are substantially storable without any time limit, since they have no tendency, contrary to diazonium compounds, to decompose chemic- 130

ally under normal or even tropical storage conditions. The stability of their aqueous dispersions is also excellent.

5 It was surprising that the dispersions of the aromatic amines were stable, even in hot alkaline sizing liquors; furthermore that they underwent drying operations before the dyestuff development without damage.

10 In both of the above-mentioned previously known sizing/dyeing processes different fastnesses, for example to washing, were obtained.

15 In the sizing-impregnation process (coupling component in the sizing liquor), the development with the diazo component is effected on the woven goods. Good fastness to washing is obtained after a post-treatment in a full width washer comprising rinsing and alkaline soaping with detergents at boiling temperature.

20 In the second process, in which the coupling component and an alkali resistant stabilized diazo compound are applied from the sizing liquor onto the warp, it appears that even after an intensive and repeated alkaline soaping treatment at boiling temperatures, only moderate fastnesses to rubbing and to washing are obtained. Also, with each household-washing, further bleeding and loss of colour depth occurs. A perceptible improvement in the fastness to washing is only obtained by an additional aftertreatment with copper-sulfate/acetic acid, in which aftertreatment the shade may change to become more dull. The thus obtained level of fastness to washing can be compared with that of sulphur vat dyes.

35 The fastness to washing of the colourations obtained by the process of the invention can be regulated by an aftertreatment; this is only related to the particular kind of pigment formation.

40 If only a hot washing is performed, after the weaving operation the remaining unfixed azo pigment on the warp thread has the tendency to spot the undyed weft yarn. This effect is sometimes desired, for example in the production of jeans. If a thorough aftertreatment is effected on a full width washing machine, comprising hot rinsing and alkaline soaping with an efficient detergent at boiling temperature in several boxes, the fastness to washing is very good and the weft yarn is not spotted.

50 Furthermore, it is also possible in the process of the invention to mix two or more dispersed amines which yield different shades when coupled with the coupling component, or to mix two or more bases having different coupling properties. By this variation different colour shades may be obtained.

60 The following Examples illustrate the invention.

#### EXAMPLE 1

65 A cotton warp is padded on a foulard at 90°C, with a liquor pick-up of 70%, with

a liquor prepared from 800 cm<sup>3</sup> of water at 95°C and 5 cm<sup>3</sup> of 32.5% sodium hydroxide solution with 5 g of the condensation product obtained from reacting naphthalene sulfonate with formaldehyde, 10 g of the Azoic Coupling Component 20 (C.I. No. 37 530) dissolved in a mixture of 10 g of ethanol, 5 cm<sup>3</sup> of 32.5% sodium hydroxide solution and 20 cm<sup>3</sup> of water at 40°C, 10 g of sodium nitrite dissolved in 30 cm<sup>3</sup> of hot water, and 14 g of a fine dispersion of the Azoic Diazo Component 13, C.I. No. 37 130 (containing 40% of the base and 15% of an anionic dispersing agent based on lignine sulfonic acid, prepared according to the information given above), diluted with 40 cm<sup>3</sup> of cold water.

The different smaller solutions are added, one after the other, to the hot main bath preparation whilst stirring vigorously adjusted to 1000 cm<sup>3</sup> with boiling water, and the goods are then padded with this liquor. Afterwards drying is effected on drying cylinders (the first ones heated only up to 90°C).

The dyestuff development is then effected by means of the sizing liquor at a sizing coat of 130% and at 90°C. The sizing liquor is prepared by stirring a solution of 35 cm<sup>3</sup> of 60% acetic acid and 10 g of crystallized sodium acetate dissolved in 40 cm<sup>3</sup> of hot water and 2 g of an anionic wetting agent based on the sodium salt of di-isobutyl-naphthalene - sulfonic acid, into a stock sizing agent comprising 60 g of potato starch and 15 g of carboxymethyl cellulose digested or dissolved in 800 cm<sup>3</sup> of hot water, and adjusting with boiling water up to a final volume of 1000 cm<sup>3</sup>; the goods are padded with this sizing liquor and dried on drying cylinders. After weaving with unbleached white weft yarn the goods are aftertreated by a warm rinsing and an alkaline soaping at boiling temperature.

Denim goods having red dyed warp yarns are obtained.

The same good effect can be obtained using a wet-in-wet development process without intermediate drying of the padded warps). Since the wet warp picks up less liquor, the sizing liquor has to be more concentrated, i.e. in proportion with the difference between the liquor pick-up of the impregnation foulard and the sizing-development foulard. The wet-in-wet sizing liquor contains, per litre: 130 g of potato starch, 33 g of carboxymethyl cellulose, 76 cm<sup>3</sup> of 60% acetic acid, and 22 g of crystallized sodium acetate; the other conditions remain the same, although the addition of the wetting agent is not necessary.

#### EXAMPLE 2

The process described in Example 1 is carried out, but using 8.4 g/l of the Azoic

Coupling Component 2 (C.I. No. 37 505) and 10.0 g/l of finely dispersed Azoic Diazo Component 48 (C.I. No. 37 235).

5 A Denim fabric having a blue warp is obtained.

WHAT WE CLAIM IS:—

10 1. A process for sizing and dyeing a warp comprising cellulose fibres, which comprises applying to the warp a hot alkaline aqueous liquor containing an azo dyestuff coupling component, an anionic protective colloid, a  
15 finely dispersed aromatic amine, and sodium nitrite, drying the warp, and subsequently applying to the warp a hot aqueous liquid containing a sizing agent, an anionic wetting agent, and a weak organic carboxylic acid or an inorganic salt that hydrolyses to give an acidic reaction.

20 2. A process as claimed in claim 1, wherein the alkaline liquor is applied to the warp by a padding process.

25 3. A process as claimed in claim 1 or claim 2, wherein the coupling component is any one of those specifically mentioned herein.

30 4. A process as claimed in any one of claims 1 to 3, wherein the aromatic amine is any one of those specifically mentioned herein.

35 5. A process as claimed in any one of claims 1 to 4, wherein the finely dispersed aromatic amine has been dispersed with an alkylaryl - sulfonate, arylsulfonate, sulfonated cresol - formaldehyde resin, formaldehyde - naphthalene sulfonic acid condensation product, lignin sulfonate or oxylignin.

40 6. A process as claimed in any one of claims 1 to 5, wherein the dispersed aromatic amine has a maximum particle size of 0.03 mm and a "medium particle size" (as herein defined) of at most 0.003 mm.

7. A process as claimed in any one of claims 1 to 6, wherein the mol-proportion

of aromatic amine to coupling component is in the range of from 1.2:1 to 1.5:1.

8. A process as claimed in any one of claims 1 to 7, wherein the acid/sizing liquor is applied to the warp by an over-padding process.

9. A process as claimed in any one of claims 1 to 8, wherein the sizing agent is starch or carboxymethyl-cellulose.

10. A process as claimed in any one of claims 1 to 9, wherein the organic carboxylic acid is formic, acetic, lactic, tartaric or succinic acid.

11. A process as claimed in any one of claims 1 to 10, wherein the weak organic carboxylic acid is used in the presence of an alkali metal salt thereof.

12. A process as claimed in any one of claims 1 to 9, wherein the inorganic salt that hydrolyses to give an acidic reaction is aluminium sulfate.

13. A process as claimed in claim 1, conducted substantially as described herein.

14. A process as claimed in claim 1, conducted substantially as described in either of the Examples.

15. A warp comprising cellulose fibres, whenever sized and dyed by a process as claimed in any one of claims 1 to 14.

16. A process for producing a cellulose fibre fabric, wherein a sized and dyed warp as claimed in claim 15 is woven with untreated or differently dyed weft yarns.

17. A cellulose fibre fabric comprising dyed warp threads and untreated or differently dyed weft yarns, whenever produced by a process as claimed in claim 16.

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